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TITLE OF THE INVENTION

HYDROGEN GENERATING APPARATUS

BACKGROUND OF THE INVENTION

The present invention relates to a hydrogen generating apparatus which uses a fuel hydrocarbon or the like and water as raw materials and gives a hydrogen gas by steam reforming of the fuel.

For producing hydrogen, there are methods of steam reforming of fuels. In these methods, fuels such as natural gas, hydrocarbons like LPG, alcohols like methanol, naphtha and the like and water are used as raw materials and the fuels are subjected to a steam reforming reaction in a reforming part or reactor equipped with a reforming catalyst to generate hydrogen. There is also provided a shifting part conventionally for shifting water and carbon monoxide since carbon monoxide is produced as a by-product in the above-described steam reforming reaction.

Further, when a steam reforming method is used for supplying hydrogen to fuel cells, particularly to a solid polymer fuel cell, a purification part utilizing a carbon monoxide oxidizing method, methanization method or the like is provided for further removal of carbon monoxide in a shifted gas passed through a shifting part. The above-described reforming part, shifting part and purification

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part are equipped with catalysts corresponding to respective reactions and the reaction temperatures differ depending on the catalysts, therefore, there is a need to heat respective catalysts to respective reaction temperatures for stable generation of hydrogen.

In such hydrogen generating apparatuses, the temperature in the reforming part is most high and the temperature lowers gradually in the order of the reforming part, the shifting part into which a reformed gas flows in and the purification part into which a shifted gas flow in since a heating part is provided only in the reforming part situated at the upstream side. Therefore, there has been adopted a constitution in which the shifting part and the purification part are heated sequentially with heat from the reforming part, for example, heat kept in reformed gas or surplus heat in the heating part.

In such constitution, however, a long time is required before the catalyst temperatures of respective reaction parts (reforming part, shifting part and purification part) are stabilized. Surely, there is no specific problem in a hydrogen generating apparatus which is usually operated in continuous mode used in a plant and the like since the operation can be effected while estimating the starting-up time. However, such constitution is not preferable in a hydrogen generating

In this reforming, higher the reaction temperature, higher the concentration of carbon monoxide (CO) generated, therefore, particularly when hydrocarbon-based fuel is used,

a CO shifting catalyst is used and CO and steam are reacted to reduce the CO concentration down to 0.1 to 1% for example.

Particularly in the case of a fuel cell which works at a lower temperature of about 100°C like a solid polymer fuel cell, there is required decrease in the CO concentration down to several ppm level, hence causing use of a CO purification catalyst which selectively oxidizes CO by addition of a trace amount of air. This catalyst has been used as a catalyst body having a form of pellet such as cylindrical, spherical and the like.

However, when a catalyst body in the form of a pellet is used, there has been a problem that since the catalyst body collapses due to heat impact in each starting up of a fuel cell and vibration in being mounted on vehicles and the like, the catalyst can not be used until the life inherent to the catalyst component due to generated need of exchange with a novel catalyst body. There has been also a possibility that a catalyst powder produced by collapsing of the catalyst body obstructs the fuel flow route of a fuel cell.

Namely, conventional hydrogen generating apparatuses have no large problem in uses wherein only stationary operation is conducted in chemical plants and the like and frequent starting up operation is not required, however

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methanizes a reformed gas, the scattered CO shifting catalyst prevents selective oxidation of CO and increases the CO concentration by a reverse shift reaction, providing a factor causing reduction in efficiency of the whole apparatus.

The third object of the present invention is to provide a hydrogen generating apparatus which eliminates influence by scatter of a catalyst body and operates in a stable manner for a long period of time, for solving the above-described problems of hydrogen generating apparatuses, in view of the above-described facts.

BRIEF SUMMARY OF THE INVENTION

described reforming catalyst, a CO shifting catalyst body and a CO purification catalyst body and in which the reforming catalyst body, the CO shifting catalyst body, the CO purification catalyst body being placed sequentially in this order from the above-described fuel feeding part toward the downstream side, wherein a fuel and water are fed to the above-described reforming part which has been heated, an oxidant gas from the above-described oxidant gas feeding part is mixed with each of the above-described reformed gas introduced into the above-described shifting part and a shifted gas obtained in the above-described shifting part and introduced into the above-described purification part, and at least a part of the above-described reformed gas and at least a part of the above-described shifted gas are oxidized respectively in the above-described shifting part and the above-described purification part.

The above-described fuel feeding part and the water feeding part may be integrated, and the CO shifting catalyst is a catalyst which allows shift reaction of water and carbon monoxide.

In this case, it is preferable that a shifting catalyst of the above-described shifting catalyst body contains as one component at least a platinum group-type catalyst.

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Further, it is preferable that a hydrogen generating apparatus has a shifting catalyst temperature measuring part which measures the temperature of the above-described shifting catalyst body and the temperature of the shifting catalyst is controlled by controlling the amount of an oxidant gas to be mixed with the above-described reformed gas.

Furthermore, it is preferable that a hydrogen generating apparatus has a purification catalyst temperature measuring part which measures the temperature of the above-described purification catalyst body and the temperature of the purification catalyst is controlled by controlling the amount of an oxidant gas to be mixed with the above-described shifted gas.

Still further, it is preferable that an oxidant gas from the above-described oxidant gas feeding part is mixed with a fuel and water from the above-described fuel feeding part and the water feeding part.

Moreover, it is preferable that a hydrogen generating apparatus has a reforming catalyst temperature measuring part which measures the temperature of the above-described reforming catalyst body and the temperature of the reforming catalyst is controlled by controlling the amount of an oxidant gas to be mixed with the above-described fuel and water.

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Furthermore, the hydrogen generating apparatus of the present invention has, for attaining the above-described third object, the above-described scatter preventing means provided at least between the above-described reforming

It is preferable that the above-described scatter preventing means is a filter and a pressure detecting apparatus which detects pressure loss caused the above-described filter is placed at the upstream side and at the downstream side of the above-described filter.

As the above-described filter, filters are exemplified constituted of fiber composed of a metal, ceramics or complex thereof. There can also be used filters composed of a metal, ceramics or complex thereof in the form of mesh, honeycomb or foam.

In the hydrogen generating apparatus of the present invention, it is preferable that the temperature of the above-described filter is higher than the temperature at which a reformed gas is methanized.

Further, it is preferable that a temperature detecting apparatus is provided at a position near the above-described filter.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

Fig. 1 is a schematic longitudinal section view showing the constitution of a hydrogen generating apparatus of one embodiment in accordance with the present invention.

Fig. 6 is a schematic constitution view of a hydrogen generating apparatus of another embodiment in accordance with the present invention.

Fig. 1 is a schematic longitudinal section view showing the constitution of a hydrogen generating apparatus

In a reforming part 2, a reforming catalyst part 2b for accommodating a reforming catalyst 2a for a steam reforming reaction is provided and it steam-reforms a fuel. Herein, as the reforming catalyst 2a, there are used, for example, catalyst prepared from platinum group noble metals and the like.

A shifting part 6 accommodates a shifting catalyst body 6a, and allows carbon monoxide in the reformed gas obtained in the reforming part 2 to shift. Further, a shifting catalyst temperature measuring part 7 is provided for detecting the temperature of the shifting catalyst body 6a. Herein, as the catalyst to be carried on the shifting

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In this constitution, air is fed from the oxidant gas-feeding part 13 through the first route 13a and the second route 13b to the reformed gas and shifted gas to be mixed. By this mechanism, the catalyst temperature in the shifting part 6 and the purification part 10 can be

increased and stabilized even if a heating part is not provided in the shifting part 6 and the purification part 10 and the heating part 4 is provided only in the reforming part 2.

For starting up a hydrogen generating apparatus at room temperature and feeding, in a stable manner, hydrogen (purified gas) containing a small amount of carbon monoxide, it is necessary that catalysts in the shifting part 6 and the purification part 10 are heated to suitable temperatures. Then, the hydrogen generating apparatus of the present invention utilizes effectively heats of the reformed gas and the shifted gas and stabilizes the catalyst temperature of each reaction part in a short period of time, irrespective of the heating part provided only in the reforming part 2.

Namely, the hydrogen generating apparatus of the present invention is characterized in that an oxidant gas such as air is previously fed and mixed not only with a shifted gas introduced into the purification part, which oxidizes carbon monoxide and decreases the amount thereof, but also with a reformed gas introduced into the shifting part.

Next, there will be illustrated more in detail how the catalyst temperature in each reaction part in the hydrogen generating apparatus of the present invention

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The reforming part 2 is heated by the heating part 4 to increase quickly the temperature of the reforming catalyst body 2b. The fuel reformed by the reforming catalyst 2a becomes a reformed gas, then, shifted in the shifting part 6 to become a shifted gas. Then, the shifted gas purifies carbon monoxide contained in the purification part 10.

In the present invention, since heat generated in the shifting catalyst body 6a and the purification catalyst body 10a are utilized, the amount of such generated heat can be controlled by the amount of air fed and the control of the catalyst temperature also becomes easy.

Further, since a large amount of hydrogen is contained in the reformed gas by a steam reforming reaction

According to Embodiment 1 of the present invention, the catalyst in each reaction part can be heated to an appropriate temperature in a shorter period of time than that in a constitution wherein the shifting part and the purification part are heated sequentially, by using only heat kept in the reformed gas, since each reaction part can be heated separately. Also, a relatively simple constitution is possible in which an oxidant gas-feeding part 13 is only added.

Example 1

The heating part 4 was allowed to operate to initiate heating of the reforming part 2. Then, a methane gas, which was a hydrocarbon, was used as a fuel, which was a raw material, and 2 mol or more water was added per 1 mol of a methane gas, and fed to the reforming catalyst 2a (catalyst prepared from platinum group-type noble metal) in the reforming part 2. The heating quantity in the heating part 4 was controlled so that the temperature of the reforming catalyst became about 700°C for proceeding of the steam reforming reaction.

Then, the resultant reformed gas was fed to the shifting part 6 filled with a platinum group-type noble metal catalyst. In the shifting part 6, the content of carbon monoxide in the reformed gas is decreased by the shifting reaction with water. It is necessary that the shifting catalyst body 6a is heated quickly to a temperature from about 200 to 350°C for proceeding the shift reaction. Then, air was fed to the reformed gas, a part of the reformed gas component was oxidized using a shifting catalyst body 6a, and the catalyst was heated to a temperature suitable for the reaction. The amount of air

to be fed was controlled based on the detected temperature by the shifting catalyst temperature measuring part, so that, in the present example, the upper limit temperature was 350°C.

Then, the shifted gas obtained in the shifting part 6 was mixed with air fed and introduced into the purification part 10. In the purification part 10, carbon monoxide is oxidized with oxygen and removed.

Also in the purification part 10, at least a part of the shifted gas component is oxidized by using a purification catalyst body 10a carrying a purification catalyst (platinum group-type oxidation catalyst), and the catalyst is heated to a temperature suitable for the reaction, similarly in the shifting part 6. The amount of air to be fed was controlled so that, in the present example, the detected temperature in the purification catalyst temperature measuring part was from 100 to 200°C.

The amounts of air fed to the shifting part 6 and the purification part 10 have to be set depending on the amount of hydrogen to be generated. In the present example as described above, by feeding air to the shifting part 6 and the purification part 10 and by heating each reaction part, the time until the catalyst temperature in each reaction part reached the temperature suitable for the reaction could be shorted to about one-fourth as compared with the

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Then, the hydrogen generating apparatus was operated to give stationary state.

In this case, in the purification part 10, carbon monoxide could be oxidized (purified) by feeding air containing oxygen at an amount corresponding to at least a half amount of carbon monoxide in the shifted gas, even if the temperature reached to 100 to 200°C.

When the amount of raw materials fed was changed up to 3-fold, the catalyst temperature changed significantly if air was not fed depending on the catalyst temperature. Resultantly, the concentration of carbon monoxide at the exit of the purification part 10 revealed a value about 10 times larger than that in stationary operation.

Fig. 2 is a schematic longitudinal section view showing the constitution of a hydrogen generating apparatus according to one embodiment of the present invention. The hydrogen generating apparatus shown in Fig. 2 has basically the same constitution as the hydrogen generating apparatus shown in Fig. 1, and effects the same operation. In this

The different parts include a point in which a third route 13c is provided on the oxidant gas-feeding part 13 and air is fed through the third route to raw materials (fuel and water) before introduced into the reforming part 2.

By this constitution, the catalyst can be heated to the temperature suitable for each reaction in each reaction part, and the time required until stable feeding of hydrogen can be further shortened.

Since the relative amount of fed hydrogen decreases by feeding air to each reaction part, it is preferable to provide sufficient heat dissipation-preventing measures to each reaction part and gas feeding route from the viewpoint of reduction in the amount of air to be fed. For example, each reaction part and gas feeding route may be covered

with a heat insulating material.

Example 2

The hydrogen generating apparatus according to Embodiment 2 described above was allowed to operate.

The apparatus was operated in the same manner as in Example 1 described above except that air was fed to raw materials before introduced into the reforming part 2 in starting up and a part of the raw materials was oxidized in the reforming part 2. It was confirmed that by feeding air to raw materials before introduced into the reforming part 2, the catalyst temperature in the reforming part 2 reached to the set temperature more quickly as compared with Example 1.

By using platinum group-type catalysts in the reforming part 4, the shifting part 6 and the purification part 10 as in the present example, oxidation with air of the reformed gas and fuel (hydrocarbon), which are raw materials, can proceed quickly.

Particularly, by adopting a constitution in which catalysts mainly composed of platinum are commonly used, recycle of the catalysts is easy in recovering catalysts. Further, reduction treatment of catalysts is not needed and oxidation of catalysts does not occur easily by mixing of air after stopping of the apparatus, leading resultantly to

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easy maintenance.

Further, catalysts other than platinum group-type catalysts may be used in the reforming part 4, shifting part 6 and purification part 10, in the range wherein the effect of the present invention is not lost. For example, catalysts suitable for respective reactions may be appropriately selected by those skilled in the art, such as nickel-type catalysts for the reforming part 4, copper-type catalysts for the shifting part 6 and gold-type catalyst for the purification part 10, and the like.

Further, the catalyst temperature for each reaction part may advantageously be set depending on the kind of the catalyst used, and as the raw material fuel, there may be used any material usually used as a raw material of steam reforming, such as, in addition to methane, natural gas, hydrocarbons such as LPG and the like, alcohols such as methanol, naphtha and the like.

According to Embodiments 1 and 2 of the present invention, a part of oxygen in air fed and raw materials or reformed gas are oxidized by using the catalyst in the reforming part, shifting part or purification part, to generate oxidation heat. This heat enables quick heating of the catalyst in each reaction part up to the temperature suitable for the reaction. Further, since oxidation heat on the reforming catalyst, shifting catalyst and

purification catalyst is utilized for heating, the amount of heat generation can be controlled by the amount of air to be fed and the catalyst temperature can be controlled easily.

Moreover, the time required until stable hydrogen feeding is obtained in starting up of the apparatus can be shortened significantly and change in the catalyst temperature in each reaction part in changing of the amount of hydrogen generated can be dealt with appropriately.

Also, a relatively simple apparatus constitution is possible in which the shifting part and the purification part need no special heating means.

Embodiment 3

Another embodiment of the hydrogen generating apparatus of the present invention will be explained below. The explanation will be made sequentially along the flow of a fuel (raw material gas) in the hydrogen generating apparatus of the present invention referring to a drawing for easy understanding.

Fig. 3 is a schematic view showing the constitution of one example of a hydrogen generating apparatus of the present invention.

In the hydrogen generating apparatus shown in Fig. 3, a fuel is introduced through a fuel feeding part 21, and

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steam is added through a water feeding part 22 for fuel reforming. A raw material gas prepared by mixing the fuel and steam is heated by passing through a flow route having a heat exchange fin 23. The raw material gas comes into contact with a reforming catalyst body 24 heated by a heating burner 25 and reacts therewith, to produce a reformed gas. In this operation, a combustion gas is discharged from an exhaust port 26. Then, the amount of CO contained in this reformed gas is reduced by a CO shifting catalyst body 27. Further, since CO is required to be removed to several ppm level for use in a solid polymer fuel cell, a small amount of an oxidant gas such as air and the like is introduced through a CO purifying oxidant gas-feeding part 28, and CO is oxidized to be removed by using a CO purification catalyst body 20. A reformed gas from which CO has been removed is fed through a reformed gas outlet 30 to a fuel cell for example.

The fuel to be introduced through the fuel feeding part 21 is not particularly restricted providing it can feed hydrogen, and examples thereof include various fuels of hydrocarbon type, ether type and alcohol type such as natural gas, coal gas, liquefied petroleum gas, propane gas, kerosene, gasoline, methanol and dimethyl ether and the like. There can also be used oil gases obtained by thermal cracking of petroleum and town gases prepared by mixing

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liquefied petroleum gas. Of them, a 13A town gas is composed of methane as a main component and can be used in the same like manner as natural gas.

In the present invention, hydrogen can be generated by reforming the above-described fuel, and as this reforming method, there can be used any reforming method such as a steam reforming method in which steam is added, a partial reforming method in which air is added, reforming methods composed of combinations thereof, and the like.

Therefore, it may be permissible that steam is added through the water feeding part 22 or a mixture of air and steam is also added, depending on the kind of the above-described reforming method.

The feeding ratio of a fuel to steam differs depending on the kind of the fuel the kind of the reforming method and the like, and it may be advantageous that the ratio is not less than the stoichiometric ratio for conversion of a fuel into CO_2 and hydrogen and within the range in which the efficiency does not decrease. Specifically, it may be advantageously from 1 to 3 in terms of the stoichiometric ratio.

When a steam reforming method is used as the reforming method, it may be advantageously within the ranges described below, for example.

Kind of fuel	Feeding amount per fuel 1
Natural gas	2 ~ 5
Propane gas	6 ~ 15
Kerosene	20 ~ 40
Gasoline	16 ~ 32
Methanol	1 ~ 2
Dimethyl ether	31 ~ 26

The term "reformation" generally means an operation to generate hydrogen from a fuel and steam or an oxidant gas (for example, oxygen) or to change the composition of a hydrocarbon as the fuel by utilizing heat or a catalyst to improve the properties and conditions thereof. In the present invention, it means that hydrogen is generated from a fuel and steam and/or an oxidant gas.

A raw material (mixed) gas composed of a fuel and steam introduced through the fuel feeding part 21 and the water feeding part 22, then, passes through a flow route equipped with a heat exchange fin 23 and comes into contact with a reforming catalyst body 24. The flow route may advantageously be constituted of a conventionally known material such as a metal like stainless steel (copper, aluminum or the like is possible in the case of lower temperature) for example, and the heat exchange fin 23 may also be constituted of a conventionally known material.

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In the present invention, this reforming catalyst is ground by an ordinary method to give a powder. The particle size of this powder is not particularly restricted providing it is in the range wherein dispersibility is not disturbed when a slurry is produced and releasing does not occur when carried on a carrier. Specifically, the range from 1 to 2 μm may be allowable, for example.

The dispersing medium which disperses a reforming catalyst body is not particularly restricted providing it can be evaporated easily after the resultant slurry is coated on a carrier. Specifically, water, alcohol and the like are exemplified, for example.

The heating temperature of the reforming carrier 24

obtained as described above when a raw material gas passes through differs depending on the kind of a fuel, the kind of the reforming catalyst and the like, and generally may be a temperature at which a fuel causes a reforming reaction generating a hydrogen gas.

Heating temperature ranges for respective kinds of fuels are exemplified below.

Kind of fuel	Heating temperature ranges
Natural gas	500 ~ 800
Propane gas	500 ~ 800
Kerosene	500 ~ 800
Gasoline	500 ~ 800
Methanol, Dimethyl ether	200 ~ 400

When a raw material gas passes through the reforming catalyst body 24, it becomes a reformed gas which usually contains CO in addition to hydrogen (for example, about 10% CO is contained when natural gas is used as a fuel and reforming is conducted at a temperature from 500 to 800°C). On the other hand, when hydrogen obtained in the hydrogen generating apparatus of the present invention is used for example in a solid polymer type fuel cell, it is necessary that the CO concentration is reduced to about several thousands ppm to 1%. Therefore, this reformed gas is

passed through a CO shifting catalyst body 27 to reduce the CO concentration in the reformed gas to about several thousands ppm to 1%.

The production method and the like of the CO shifting catalyst body 27 are the same as those in the case of the above-described reforming catalyst body 24 except that the kinds of catalysts used are different.

The CO shifting catalyst herein used is not particularly restricted providing it has a function to cause a reaction between CO and steam to give CO₂ and hydrogen, and examples thereof include Cu-Zn-type catalysts, Fe-Cr-type catalysts and the like, usually used. Namely, the "CO shifting" herein referred to means a procedure in which CO and steam are reacted to give CO₂ and hydrogen, and the high concentration (for example, 10%) of CO is lowered to the low concentration (for example, 1 to 2% or lower).

Further, when methanol, dimethyl ether and the like are used as the fuel, reforming can be conducted at relatively lower heating temperature and the concentration of CO contained in the reformed gas becomes relatively lower. In such a case, the CO shifting catalyst body 27 may be eliminated and a CO purification catalyst body 29 described later is only provided.

Further, when hydrogen is used in a solid polymer

fuel cell, it is said desirable that the CO concentration is reduced to several ppm level. Therefore, in the hydrogen generating apparatus of the present invention, a reformed gas which has passed through the CO shifting catalyst body 27 is passed through a route c to reach the CO purification catalyst body 9, to oxidizing and removing CO contained in a trace amount. In this procedure, oxygen is necessary for oxidation of CO and, therefore, oxidant gas-feeding part for purification 28 is provided on the way of a route from the shifting catalyst body 27 to the purification catalyst body 29, a reformed gas which has passed through the CO shifting catalyst body 27 are allowed to contact together with air to the shifting catalyst body 27.

The production method and the like of the CO purification catalyst body 29 are the same as those in the case of the above-described reforming catalyst body 24 except that the kinds of catalysts used are different. The CO purification catalyst herein used is not particularly restricted providing it has a function to cause selective oxidation of CO contained in the reformed gas or a function to cause a reaction between CO and hydrogen for methanization, and examples thereof include Pt-type catalysts, Ru-type catalysts and the like carried on alumina. When hydrogen obtained from the hydrogen

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generating apparatus of the present invention is used in a fuel cell which can operate even when it contains several hundreds to several thousands ppm of CO, the CO purification catalyst body 9 can be eliminated. A reformed gas which has passed through the CO purification catalyst body 29 thus obtained can be taken from the reformed gas outlet 30 and fed to, for example, a fuel cell and the like.

In the hydrogen generating apparatus of the present invention, it is preferable that outer sides of chambers, flow routes and the like containing catalyst bodies are covered with a heat insulating material.

Further, since the reforming catalyst body 24, the CO shifting catalyst body 27 and the CO purification catalyst body 29 are different in the optimum temperature distribution and heat conducting condition, it is also effective that separate materials are selected for use from heat-resistance inorganic materials, metal materials and high heat-conductive inorganic materials, such as use of a metal carrier having a honeycomb structure excellent in heat-conductivity for the reforming catalyst body 24, used of a cordierite carrier having a honeycomb structure for the CO shifting catalyst body 27 and the CO purification catalyst body 29, and the like.

Further, when a carrier having a honeycomb structure is used, composite-forming in the same catalyst body may

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also be an effective means for improving temperature distribution, such as placing of a metal rod in the center part thereof, constitution of the upstream part and the downstream part with different materials, and the like.

When air and steam are added simultaneously, intermediate properties between steam reforming and partial reforming are obtained.

The following examples will illustrate the present invention below, but do not limit the scope of the present invention.

Pelletized catalysts for reforming, CO shifting and CO purification were respectively ground (particle size: about 1 μ m), and dispersed in water in a ratio of catalyst component:water of 1:2 (by weight) and made into slurries. These slurries were coated on carriers made of cordierite having a honeycomb structure, to obtain a reforming catalyst body 24, a CO shifting catalyst body 27 and a CO purification catalyst body 29.

The composition of the produced gas excepting steam after passing through the reforming catalyst body 24 was measured by gas chromatography to find about 80% hydrogen, about 12% CO, about 8% carbon dioxide and 500 ppm methane.

When this reformed gas was passed through the CO shifting catalyst body 27, the CO concentration became about 3000 ppm, and further, air was introduced through an oxidant gas feeding part 28 so that the oxygen

concentration reached 2% and was reacted by using the CO purification catalyst body 29 to find a CO concentration of 5 ppm.

The hydrogen generating apparatus was stopped once, then, started. Further, the stopping and starting operation was repeated 1500 times and the reformed gas composition was measured to find that methane concentrations was 800 ppm after passing the reforming catalyst body 24, about 4500 ppm after passing the CO shifting catalyst body 27, and 7 ppm after passing the CO purification catalyst body 29.

Example 4

The hydrogen generating apparatus obtained in Example 3, a fuel cell and a driving motor were connected and mounted on an automobile, and a 100000 km driving test was conducted.

After the driving, the composition of the reformed gas was measured by gas chromatography in the same manner as in Example 3 to find that a methane concentration was 1000 ppm after passing the reforming catalyst body 24, a CO concentration was about 4800 ppm after passing the CO shifting catalyst body 27, and a CO concentration was 9 ppm after passing the CO purification catalyst body 29.

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Example 5

The hydrogen generating apparatus was operated in the same manner as in Example 3 except that a Fe-Cr-Al type stainless steel was used instead of cordierite as the material of a carrier having a honeycomb structure.

The composition of the produced gas excepting steam after passing through the reforming catalyst body 24 was measured by gas chromatography to find about 80% hydrogen, about 12% CO, about 8% carbon dioxide and 300 ppm methane.

When this reformed gas was passed through the CO shifting catalyst body 27, the CO concentration became about 2500 ppm, and further, air was introduced through the oxidant gas feeding part 28 so that the oxygen concentration reached 2% and was reacted by using the CO purification catalyst body 29 to find a CO concentration of 3 ppm.

The hydrogen generating apparatus was stopped once, then, started. Further, the stopping and starting operation was repeated 1500 times and the reformed gas composition was measured to find methane concentrations of 700 ppm after passing the reforming catalyst body 24, of about 4000 ppm after passing the CO shifting catalyst body 27, and of 6 ppm after passing the CO purification catalyst body 29.

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Pelletized catalysts for reforming, CO shifting and CO purification used in Example 3 were filled, without grinding, into chambers as shown in Fig. 4, and a desulfurized town gas was introduced through a fuel feeding part 31 at a flow rate of 50 liter per minute and steam was introduced through a water feeding part 32 at a flow rate of 150 liter per minute.

When this reformed gas was passed through a CO shifting catalyst body 37, the CO concentration became about 3500 ppm. Further, when air was introduced through an oxidant gas feeding part 38 so that the oxygen concentration reached 2% and was reacted by using a CO purification catalyst body 39, a CO concentration became 6 ppm.

Then, the hydrogen generating apparatus was stopped, then, started. Further, the stopping and starting operation was repeated 1500 times and the reformed gas

Comparative Example 2

After the driving, the composition of the reformed gas was measured by gas chromatography to find a methane concentration of 20000 ppm after passing the reforming catalyst body 34, a CO concentration of about 16000 ppm after passing the CO shifting catalyst body 37, and a CO concentration of 9000 ppm after passing the CO purification catalyst body 39.

The palletized catalyst body was taken out of the reaction chamber and observed to find that the palletized catalyst collapsed significantly to be a size about a half

of the original size.

As is apparent from the comparison between the evaluation results of examples and comparative examples, according to Practical Embodiment 3 of the present invention, a hydrogen generating apparatus can be provided which elongates the life of a catalyst, suppresses influences by stopping of operation of an apparatus, repetition of operation and vigorous vibration, and operate for a long period of time in a stable manner.

Embodiment 4

Embodiment 4 of the present invention will be illustrated referring to drawings below.

Fig. 5 is a schematic constitution view of Embodiment 4 of a hydrogen generating apparatus of the present invention.

In the hydrogen generating apparatus shown in Fig. 5, a fuel is introduced through a fuel feeding part 41 and steam is added through a water feeding part for fuel reforming 42. A raw material gas prepared by mixing the fuel and steam passes through a flow route having a heat exchange fin 23. The raw material gas comes into contact with a reforming catalyst body 44 heated by a heating burner 45 and reacts therewith, to produce a reformed gas. In this operation, a combustion gas is discharged from a

discharging port 46. Then, the amount of CO contained in this reformed gas is reduced by a CO shifting catalyst body 47. Further, since CO is required to be removed to several ppm level for use in a solid polymer fuel cell, a small amount of air is introduced through a CO purifying oxidant gas-feeding part 48, and CO is oxidized to be removed by using a CO purification catalyst body 49. A reformed gas from which CO has been removed is fed through a reformed gas outlet 50 to a fuel cell for example.

A first filter 51 and a second filter 52 are placed respectively at the downstream side of the reforming catalyst body 46 and the CO shifting catalyst body 47.

For keeping the reaction vessel at constant temperature, parts of the apparatus may be covered with heat insulation materials. The catalyst body may be conventional one, and it is preferable to use a Ni catalyst for the reforming catalyst body, a Cu-Zn catalyst for the CO shifting catalyst body, and a Pt catalyst for the CO purification catalyst body, respectively.

Examples of the fuel for generating a reformed gas are town gas (natural gas), propane, kerosene, gasoline, methanol, dimethyl ether and the like. As the reforming method, there are a steam reforming method in which steam is added, a partial reforming method in which air is added, reforming methods composed of combinations thereof, and the

Herein, a case in which natural gas is used as the fuel gas and steam-reforming is conducted will be described as a typical example. However, reforming methods using other fuel or composed of partial reforming or a combination of partial reforming and steam reforming can be applied to the present method though the composition of the resulting reformed gas differs slightly and the temperature condition in reforming changes.

A fuel is introduced through a fuel feeding part 41 and steam in an amount of about 3-fold based on the fuel is added through a water feeding part 42. The mixed raw material gas is heated by a heating burner 44, and comes into contact with a reforming catalyst body 46 which has been heated to about 500 to 800°C and reacts, to produce a reformed gas. Since this reformed gas contains CO in an amount of about 10% in addition to hydrogen, the concentration of carbon monoxide is reduced to about several thousands ppm to 1% by using a CO shifting catalyst body 47. Further, when the resulted hydrogen gas is used in a solid polymer fuel cell, it is necessary that the CO concentration is reduced to about several ppm, therefore, a

As described above, in the case of a fuel cell system for automobile uses or domestic uses, frequent starting up and stopping should be repeated, and in this operation, significant heat impact is imparted to each catalyst body. Particularly in the case of automobile uses, vibration is applied to catalyst bodies in driving. If an apparatus is operated for a long period of time under such conditions, a catalyst body is cracked gradually and fine powder may be formed. At that time, there is no significant influence on the reactivity of a catalyst body itself, however, a catalyst powder fallen from the catalyst body flies or scattered to the downstream side. When a catalyst powder is thus scattered, the powder is collected mainly onto a catalyst body situated at the downstream side of the catalyst body caused the scattering. Specifically, the reforming catalyst is collected on a CO shifting part, and a CO shifting catalyst is collected on a CO purification part.

Usually, since a catalyst which can be applied as a reforming catalyst for a hydrocarbon acts as a

On the other hand, when a first filter 51 and a second filter 52 are placed respectively at the downstream side of a reforming catalyst body and a CO shifting catalyst body, as in Embodiment 4, the apparatus can be operated for a long period of time in a stable manner without a scattered catalyst powder being collected on a CO shifting catalyst body and a CO purification catalyst body as described above.

In this case, it is preferable that the first filter 51 at the downstream side of the reforming catalyst body 46 is set at a temperature wherein the methanization reaction

As the above-described first filter 51 and second filter 52, filters can be used constituted of fiber composed of a metal, ceramics or complex thereof. It is also preferable to use filters in the form of mesh, honeycomb or foam composed of a metal, ceramics or complex thereof.

These are structures which can collect a scattered

catalyst particle, and fully cheap materials under use conditions. There is an effect that the surface is porous and a half or more of the catalyst scattered before passing through is collected.

In the practical embodiment, the first filter 51 and second filter 52 are placed in ordinary narrow routes, however, the route at the filter part can be thickened so that the filter area increases, and the filter can be bent to suppress increase in pressure loss of the filter due to clogged catalysts.

+ Since pressure loss increases by clogging of the filter, it is preferable to place pressure detecting instruments at the upstream side and the downstream side of the first filter 51 and the second filter 52. When the pressure loss increases, pumps for feeding fuels and the like are loaded, decreasing efficiency. Therefore, by detecting pressures before and after the filters, pressure loss by the first filter 51 and the second filter 52 is measured, and when it reaches the pre-determined standard value, the filter can be exchanged for operation of the hydrogen generating apparatus for a long period of time in a stable manner.

In the present embodiment, since it is required that a solid polymer cell is used as the fuel cell and the CO concentration is reduced to ppm level, a CO purification

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catalyst body may be dispensable if the fuel cell part acts with a reformed gas containing CO in an amount from several hundreds to several thousands ppm, as described in the case wherein a reforming catalyst body, a CO shifting catalyst body and a CO purification catalyst body are all provided.

When a fuel such as methanol and dimethyl ether is used, reforming is possible at a lower temperature around 300°C, and the CO concentration after reforming relatively decreases, therefore, there is also a case in which operation is possible only with a CO purification catalyst body even without employing a CO shifting catalyst body. In this case, since a catalyst similar to a CO shifting catalyst, for example, a copper-zinc-type catalyst is used as the reforming catalyst, the scattered catalyst powder has the same influence with the scattered CO shifting catalyst of the present example, and it is preferable to place a filter downstream of the reforming catalyst body.

In the present embodiment, an example in which a fuel is steam-reformed is described, however, when partially reforming is conducted while adding air instead of steam, the proportion of hydrogen contained in the reformed gas decreases, and a combustion reaction occurs simultaneously with reforming on the catalyst and heating of the catalyst body becomes easy. Still more, when air and steam are added simultaneously, intermediate properties between the

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in Fig. 6, thermocouple 73 and measuring apparatus 74 connected to the thermocouple 73 are placed near a first filter 71, and the first filter 71 at the downstream side of a reforming catalyst body is set at a temperature wherein the methanization reaction progresses substantially. Most of the actions and effects of the present embodiment are the same as those in Embodiment 4. Therefore, the present embodiment will be illustrated mainly on different parts.

Fig. 6 is a schematic constitution vies of the present embodiment. The first filter 71 is placed near the intermediate part between a reforming catalyst body 66 and a CO shifting catalyst body 67, and the temperature thereof is in the range from 400 to 500°C which is also sandwiched between them. When the first filter 71 collects the scattered catalyst from the reforming catalyst body 66, heat generation occurs since the temperature of the first filter 71 is a temperature at which the methanization proceeds. The heating value is in proportion with the amount of the scattered catalyst collected on the first filter 71, and by detecting the temperature by thermocouple 73 placed near the first filter 71, the amount of the scattered catalyst collected on the first filter 71 can be estimated. When the temperature of the first filter 71 reached the standard value previously determined, if the

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filter is exchanged, the hydrogen generating apparatus can be operated for a long period of time in a stable fashion.

In the present embodiment, the thermocouple are placed near and at the downstream of the filter as shown in Fig. 6, however, the thermocouple can be placed near and at the upstream side, on the side face or outside of the tube, depending on the constitution. As the temperature detecting apparatus, there can also be used detecting means which detect temperature giving signals, such as thermistors, bimetals and the like.

The following examples illustrate Embodiments 4 and 5 of the present invention more specifically, but do not limit the scope thereof.

Example 6

A reforming catalyst body 46 composed of a Ni-type reforming catalyst, a shifting catalyst body 47 composed of a Cu-Zn-type CO shifted catalyst, and a purification catalyst body 49 composed of a Pt-type CO selective oxidation catalyst were respectively filled in a hydrogen generating apparatus shown in Fig. 5. A first filter 51 and a second filter 52 composed of stainless metal fiber having a line diameter of $0.1 \mu\text{m}$ were respectively placed at downstream side of the reforming catalyst body 46 and the CO shifting catalyst body 47. A de-sulfurized town gas

The hydrogen generating apparatus was stopped once, then, started. Further, the stopping and starting operation was repeated 1500 times and the reformed gas composition was measured in a like manner. The methane concentrations in the gas before and after passing the first filter 51 and the methane concentrations in the gas after passing the CO shifting catalyst body 47 were all 0.06%. The CO concentration of the gas after passing the CO purification catalyst body 49 was 9 ppm. The pressures before and after the first filter 51 and the second filter 52 were measured and pressure losses were calculated based

on the original pressures to find they were 20 mAq and 40 mAq, respectively. The filters were removed from the apparatus and weights of the catalyst powder adhered were measured to find that the increase in weight of the first filter 51 was 12 g and that of the second filter 52 was 38 g.

Example 7

The hydrogen generating apparatus of Example 5, a fuel cell and a driving motor were connected and mounted on an automobile, and a 20000 km driving test was conducted. After the driving, the composition of the reformed gas was measured by gas chromatography in the same manner as in Example 5 to find that the methane concentrations in the gas before and after passing the first filter 51 and the methane concentrations in the gas after passing the CO shifting catalyst body 7 were all 0.08%. The CO concentration of the gas after passing the CO purification catalyst body 4 was 10 ppm.

Example 8

As shown in Fig. 6, a first filter 71 was placed at the intermediate part between a reforming catalyst body 66 and a CO shifting catalyst body 67. Thermocouple 73 were placed so that they were in contact with the first filter

A de-sulfurized town gas was introduced through a fuel feeding part 61 at a flow rate of 50 liter per minute and steam was introduced through a water feeding part 62 at a flow rate of 150 liter per minute. The composition of the gas after passing through the reforming catalyst body 66 was found to include about 80% hydrogen, about 11% CO, about 9% carbon dioxide and 0.05% methane. Further, the composition of the gas after passing a CO shifting catalyst body 67 included 0.05% methane and 0.3% CO, respectively. Further, the CO concentration of the gas after passing a CO purification catalyst body 69 was 8 ppm.

The hydrogen generating apparatus was stopped once, then, started in the same manner as in Example 5. Further, the stopping and starting operation was repeated 1500 times and the reformed gas composition was measured. The methane concentrations in the gas after passing the reforming catalyst body 66 was 0.06%, and the methane concentration of the gas after passing the reforming catalyst body 66 was 5.5%. The CO concentration of the gas after passing the CO shifting catalyst body 27 was 0.3%, and the CO concentration of the gas after passing the CO purification catalyst body 29 was 10 ppm. The temperature of the first filter 71 was compared with the original value to find a

increase of 15°C. The first filter 71 was removed from the apparatus and weight of the catalyst powder adhered was measured to find that the weight of the catalyst powder adhered to the first filter 71 was 12 g.

Then, the first filter 71 was changed to a new one, and the hydrogen generating apparatus was started up again. The methane concentration of the gas before and after passing the first filter 71 and the methane concentration of the gas after passing the CO shifting catalyst body 27 were each 0.06%. The CO concentration of the gas after passing the CO purification catalyst body was 9 ppm.

Comparative Example 3

The first filter 51 and the second filter 52 were removed in Example 5 and town gas and water were reacted. A de-sulfurized town gas was introduced through the fuel feeding part 41 at a flow rate of 50 liter per minute and steam was introduced through the water feeding part 42 at a flow rate of 150 liter per minute, and they were reacted. The composition of the reformed gas was found to include about 80% hydrogen, about 11% CO, about 9% carbon dioxide and 0.05% methane. Further, the composition of the gas after passing the CO shifting catalyst body 7 included 0.05% methane and 0.3% CO, respectively. Further, the CO concentration of the gas after passing the CO purification

catalyst body 9 was 8 ppm.

As is apparent from the comparison between the evaluation results of Examples 6 to 8 and Comparative Example 3, the hydrogen generating apparatuses of Practical Embodiments 4 and 5 prevents influences by stopping of operation of an apparatus, repetition of operation and scatter of a catalyst due to vigorous vibration, and can be operated for a long period of time in a stable manner.